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ABSTRACT

The tremendous domestic reserves of phosphate rock together with the large annual production of normal superphosphate from phosphate rock have made the recovery of the small amounts of uranium (0.01 to 0.02 percent) in phosphate rock during the production of superphosphate an important problem. At current superphosphate production rates there exists a uranium potential of approximately 1000 tons per year.

In most phosphate rocks 80 percent or more of the phosphorus content is unavailable to plant life. Normal superphosphate is produced by the reaction of sulfuric acid and phosphate rock to convert the phosphorus to a form available to plant life. The purpose of this investigation was to make a quantative study of the effect of phosphate rock particle size on the recovery of uranium during the production of normal superphosphate.

Florida land pebble phosphate rock was used in this work. The uranium content of this rock was 0.0184 percent U_3O_8. Phosphate rock particle sizes of 62, 77, and 92 percent through 200 mesh were studied. Both a 1.81 and a 2.50 acidulation ratio (pounds of 100 percent sulfuric acid per pound of P_2O_5) were studied at each particle size. Industrially, a 1.81 acidulation ratio is used for the production of normal superphosphate; a 2.50 acidulation ratic is used for phosphoric acid production.

The acidulation of the phosphate rock to superphosphate and the extraction of the uranium into the solvent were accomplished simultaneously by adding the sulfuric acid to a slurry of the rock and solvent. The solvent used was a 10 percent di-octyl pyrophosphoric acid solution in normal heptane. A solvent to rock ratio of 0.8 milliliters per gram was used throughout; 60 percent sulfuric acid was also used throughout. The most favorable uranium recovery was 73 percent.

When the 2.50 acidulation ratio was used an additional quantity of rock was added to the reaction products, after the solvent had been removed, to reach an overall 1.81 acidulation ratio. Superphosphate was thus produced. This additional rock was not finely ground as it did not contact the solvent for uranium extraction.

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[1] This report is based on an M.S. thesis by William Wayne Davis submitted December, 1955 at Iowa State College, Ames, Iowa. This work was performed under contract with the Atomic Energy Commission.

It was found that the uranium recovery obtained in a 30 minute reaction-extraction increased significantly with a decreasing particle size. The process based on an initial over-acidulation ratio (2.50) did not appear to have any advantage over the process based on the normal acidulation ratio (1.81).

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INTRODUCTION

Importance of Problem

Phosphorus is one of the most important plant foods. Nearly all of the farming lands of the United States are deficient to some extent in phosphorus content (6). For this reason phosphate fertilizers are applied more often and in greater quantities than any other synthetic plant food (13). To supply the raw material for the production of these fertilizers large tonnages of phosphate rock are mined each year. In recent years the United States has mined approximately 10 million long tons of phosphate rock annually (13). The main sources of this are the Florida and Tennessee phosphate rocks and the phosphoria formations of the western states of Idaho, Montana, Utah, and Wyoming. Present estimates of the reserves of phosphate rock in the United States are greater than 13 billion tons (6).

Florida and western states phosphate rocks have a uranium content varying from 0.01 to 0.02 percent; the Tennessee phosphate rock does not contain uranium. Some of this uranium is now being recovered during the production of wet process phosphoric acid (12). However, 65 percent of the phosphate rock mined in the United States is used for the production of normal superphosphate (6). Using this figure, the annual production of phosphate rock, and assuming an average uranium content for all phosphate rock of 0.015 percent gives a potential source of approximately 1000 tons of uranium per year. It is this great annual potential together with the tremendous reserves of phosphate rock that make the recovery of uranium from normal superphosphate important.

Phosphate rock consists mainly of insoluble fluorapatite ($Ca_{10}F_2(PO_4)_6$) and varying amounts of other compounds of calcium, aluminum, iron, silica, and fluorine (7). It is the custom of the fertilizer industry to express phosphorus content as P_2O_5. The Association of Official Agricultural Chemists (3) prescribes a method for analysing the P_2O_5 content of any phosphate rock or superphosphate sample. This procedure determines the total, the water soluble, the citrate soluble, and the citrate insoluble portions of the P_2O_5. The total P_2O_5 should equal the sum of the latter three. The water soluble and citrate soluble portions are considered to be available to plant life. Percent conversion is defined as the available P_2O_5 divided by the total P_2O_5, multiplied by 100. In phosphate rock, phosphorus is available to plant life to a limited extent only. A high quality phosphate rock contains 30 to 35 percent total P_2O_5. Only about 20 percent of the P_2O_5 is normally available to plant life. After processing to superphosphate, however, 90 to 100 percent is available.

To convert the phosphorus in the fluorapatite lattice to an available state it is necessary to destroy the lattice structure (5). The uranium is thought to be an intimate part of this lattice and therefore the fluorapatite lattice must also be destroyed to make the uranium amenable to extraction (1). Thus the additional P_2O_5 conversion caused by the reaction to superphosphate is considered a criterion of the amount of uranium available for extraction (14).

Superphosphate is produced by the reaction of sulfuric acid with phosphate rock. This reaction essentially breaks down the lattice structure of the rock. The overall reaction may be represented as:

$$Ca_{10}F_2(PO_4)_6 + 7H_2SO_4 + 3H_2O \longrightarrow 3Ca(H_2PO_4)_2 \cdot H_2O + 7CaSO_4 + 2HF.$$

According to Andresen (1), after the reaction between the phosphate rock and the sulfuric acid is completed the uranium may be in a hydrated uranyl sulfate form -- $UO_2SO_4 \cdot 3H_2O$. The uranium extraction into the organic solvent is carried on at the same time the acidulation reaction is proceeding. This is done by adding the sulfuric acid to a slurry of the phosphate rock and solvent.

The ratio of acid to rock, called acidulation ratio, is an important variable as it controls the degree and the rate of conversion of P_2O_5 to an available form. The acidulation ratio may be defined as pounds of 100 percent sulfuric acid per pound of P_2O_5. A common industrial acidulation ratio for manufacture of superphosphate is 1.81 pounds of 100 percent sulfuric acid per pound P_2O_5; for phosphoric acid manufacture a common acidulation ratio is 2.50. Both a 1.81 and a 2.50 acidulation ratio were studied in this investigation. The 2.50 acidulation ratio was maintained only while uranium extraction was taking place. After the uranium solvent was removed, additional rock was added to reach a 1.81 acidulation ratio.

The purpose of this investigation was to make a quantitative study of the effect of phosphate rock particle size on the recovery of the uranium from phosphate rock during the production of normal superphosphate.

Previous Work

There has been little work done on the effect of phosphate rock particle size on the extraction of uranium. A. W. Andresen in work done at Ames Laboratory, found that uranium recovery did increase with decrease in particle size (2). However, no quantitative trend could be established from his limited data. Using a 1.81 acidulation ratio, he made an extraction at three different particle sizes.[1] The results of these runs are shown in Table 1.

Other work (9, 10, 11, 13) has shown that the rate of formation of superphosphate depends on particle size. Also, Kearns determined that conversion

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[1] Other conditions of these runs were a 10 minute reaction-extraction time, 200 milliliters of 10 percent O.P.P.A. as solvent, 60 percent sulfuric acid, and 250 grams of phosphate rock. He does not report whether a suspension was formed or not.

to available P_2O_5 increased with decreasing particle size until a maximum conversion was reached at 30 to 40 microns (8).

Thus there was evidence that a decreasing particle size was beneficial to P_2O_5 conversion; it appeared likely that it was also beneficial to uranium recovery. The problem, then, was resolved to obtain conclusive experimental data which would correlate phosphate rock particle size with uranium recovery.

Table 1. Previous work on phosphate rock particle size in regard to uranium extraction[a]

Phosphate rock particle size Percent through 200 mesh	Uranium recovery Percent
62.4	51
72.7	58
100	57

[a]Adapted from Andresen (2).

MATERIALS AND PROCEDURES

Materials

The phosphate rock used in this work was Florida land pebble rock. The rock, R-3, was the third lot taken from a sample of Florida rock that the Iowa State College Engineering Experiment Station had obtained from the Davison Chemical Corporation in Perry, Iowa. Andresen (1) gives a complete analysis of the first two lots, R-1 and R-2. Using the fluorimetric procedure described in Analytical Procedures, the uranium content of rock R-3 was determined to be 0.0184 percent U_3O_8. Using the method of the A.O.A.C. (3) the total P_2O_5 content was determined to be 35.3 percent.

Screen analyses of the rock at each degree of fineness are shown in Table 2. The screen analyses were made by shaking a 25 gram sample in a Tyler Ro-Tap for 30 minutes. The rock was ground in a disk grinder. To obtain the 77 percent through 200 mesh rock, the original 62 percent rock was put through the grinder once. To obtain the 92 percent through 200 mesh rock, the 77 percent rock was put through the grinder an additional two times.

The 60 percent sulfuric acid used in acidulating the phosphate rock was obtained by dilution of a commercial C.P. grade acid manufactured by Baker and Adamson. This assayed between 95.5 and 96.5 sulfuric acid.

Table 2. Screen analyses of phosphate rock R-3
(30 minutes in Tyler Ro-Tap)

Tyler standard screen mesh range	Rock R-3		
	Percent of total sample		
	62 percent	77 percent	92 percent
+ 100	14.4	5.6	0.2
- 100 + 150	5.6	7.8	2.0
- 150 + 200	18.0	9.8	5.7
- 200 + 270	6.4	5.2	15.0
- 270	55.6	71.7	77.1
Total through 100 mesh	85.6	94.5	99.8
Total through 150 mesh	80.0	86.7	97.8
Total through 200 mesh	62.0	76.9	92.1

The uranium solvent, di-octyl pyrophosphoric acid (O.P.P.A.), was prepared in the laboratory fresh for each use. The O.P.P.A. was obtained from the reaction between P_2O_5 and capryl alcohol in normal heptane. The capryl alcohol was a 95 percent grade obtained from the Rohm and Haas Company. Andresen lists its physical properties (1). Reagent grade powdered P_2O_5 was used. The diluent, normal heptane, was a commercial grade obtained from the Phillips Petroleum Company.

Procedure for Preparation of Di-Octyl Pyrophosphoric Acid

The O.P.P.A. was prepared fresh for each extraction from the reaction between one mole of P_2O_5 and two moles of capryl alcohol:

$$2\ ROH + P_2O_5 \longrightarrow \begin{matrix} & O & O & \\ RO-P-O-P-OR. \\ & O & O & \\ & H & H & \end{matrix}$$

The R group represents the normal octyl group. Due to the extreme deliquescent nature of the P_2O_5 it was necessary to weigh it rapidly into a suitable diluent. Normal heptane was used as the diluent because after the extraction it could be recovered from the superphosphate by drying below the P_2O_5 reversion temperature and because it acted as a suitable solvent for the O.P.P.A. (14).

To prepare the O.P.P.A. solution, the phosphorus pentoxide and capryl alcohol in normal heptane were violently agitated for 15 minutes in a Waring blendor. The reaction was highly exothermic; the reaction products reached a temperature of about 70°C. The Waring blendor was the normal household piece of equipment. The quantity of n-heptane used depended on the O.P.P.A. concentration desired. In this work a 10 percent O.P.P.A. solution in n-heptane was used throughout.

The solvent was always used the same day it was prepared (within 12 hours in every case). Andresen has made a study of the solvent's stability, the equilibrium K values between the O.P.P.A. solvent and aqueous uranyl nitrate solutions, and the relation between O.P.P.A. concentration and uranium recovery (1).

Acidulation and Extraction Procedures

The reaction of the phosphate rock with sulfuric acid to produce superphosphate and the extraction of the uranium into the solvent took place simultaneously. A slurry was made of 250 grams of phosphate rock and 200 milliliters of 10 percent O.P.P.A. in normal heptane in a one liter beaker. Then, for a 1.81 aciduation ratio, 178 milliliters of 60 percent sulfuric acid were added to the slurry over a time interval of 10 minutes while mixing was effected with a Sunbeam Mixmaster. This corresponds to a rate of 0.297 milliliters per second which was held constant by a small rotameter (14). The total mixing time, including the acid addition time, was 30 minutes. At the end of the 30 minute mixing time samples were taken for P_2O_5 analysis. Then as much solvent as possible was decanted off the superphosphate was washed with three 100 milliliter normal heptane washes. After the final decantation the wet superphosphate was transferred to a Buchner funnel under vacuum where additional liquid was recovered. This method accounted for 70 to 80 percent of the solvent and wash combined. This is the uranium-bearing phase. The superphosphate was then spread out in an enamel pan open to the atmosphere in a layer 1/4 to 1/2 inch thick. It was allowed to cure thusly for four weeks. The combined solvent and wash (the organic extract) was stored in an Erlenmeyer flask until analysed.

For a 2.50 acidulation ratio, 246 milliliters of 60 percent sulfuric acid were added to the slurry of 250 grams of rock and 200 milliliters of 10 percent O.P.P.A. over time intervals of 10 minutes and 13.8 minutes. These correspond to rates of 0.410 and 0.297 milliliters per second, respectively. The washing procedure was the same as for the 1.81 acidulation ratio. After the Buchner filtration, however, the solid phase was returned to the beaker along with an additional 95 grams of phosphate rock. It was not necessary for this additional phosphate rock to be ground finer than 50 to 60 percent through 200 mesh since it did not contact the solvent. The liquid phase was separated into an organic and an aqueous phase. The aqueous phase was mostly phosphoric acid, the result of using the 2.50 acidulation ratio. The organic phase was again stored for analysis. The aqueous phase, usually about 40

milliliters, was returned to the beaker containing the wet solid and the additional 95 grams of phosphate rock where mixing was continued for five minutes. It was this additional rock which reduced the overall acidulation ratio from 2.50 to 1.81. The resulting superphosphate was again cured in an enamel pan.

Analytical Procedures

The digestion and extraction of all samples for P_2O_5 analyses followed the procedure outlined by the Association of Official Agricultural Chemists (3). The samples were read on a Model DU Beckmann spectrophotometer. The color agent used was the ammonium phosphomolybdovanadate yellow color complex prepared by the method of Bridger, Boylan, and Markey (4). The standard curve for the spectrophotometer was developed by A. W. Andresen (1).

All uranium analyses for phosphate rock, superphosphates, and solvents were made by the fluorimetric procedure. A complete discussion of the fluorimetric analysis of uranium is given by Andresen (1). A method similar to Andresen's (1), but modified by Wall (14), was used in this work. Briefly, the procedure consisted of dissolving a known weight of sample containing uranium in nitric acid, thus forming uranyl nitrate. Then a micro aliquot (to reduce the amount of quenchers) of this solution was fused with a fluoride flux to form a phosphor disk. The intensity of the fluorescence of the disk was read with a fluorimeter. Through a standard curve which relates fluorimeter reading to uranium concentration, the uranium content in the original sample was determined. The procedure for analysis of the solvent was simplified by the presence of the uranium in solution. A micro aliquot of the solvent was fused with fluoride flux and read on the fluorimeter. The standard curves for solvent and superphosphate analyses were developed by Wall (14); that for the analysis of phosphate rock by the author.

The fluorimeter used in these procedures was a Galvanek-Morrison reflection type manufactured by the Jarrell-Ash Company. The fluoride flux consisted of 9 percent sodium fluoride, 45.5 percent sodium carbonate, and 45.5 percent potassium carbonate. The fusions were made for eight minutes at 650°C. in 99.9 percent pure gold dishes.

EXPERIMENTAL RESULTS AND DISCUSSION

In the usual industrial process for making normal superphosphate, phosphate rock is ground to 55 to 60 percent through 200 mesh (6). In the United States Raymond mills are generally used to grind the rock (6). These roller mills combine pulverizing and air separation in one unit. Their capacities vary from 4 to 20 tons per hour.

In this work a disk grinder was used. Phosphate rock particle sizes of 62, 77, and 92 percent through 200 mesh were studied. At each degree of fineness both a 1.81 and a 2.50 acidulation ratio were studied. The total reaction time, including the time interval over which the acid was added, was 30 minutes. At the 2.50 acidulation ratio two different acid addition rates were studied. In every case the runs were made in triplicate.

The uranium extraction and phosphate rock acidulation took place simultaneously by adding the sulfuric acid to a slurry of the rock and solvent. The solvent used was a 10 percent di-octyl pyrophosphoric acid solution in normal heptane. Throughout all the runs a total solvent to phosphate rock ratio of 0.8 milliliters per gram was used.

The advantage of further grinding is that smaller particles have greater surface areas. One of the principal products formed in the reaction of the rock to superphosphate is insoluble calcium sulfate. It is thought that the calcium sulfate formed a layer or somewhat loose coating around the rock particle. This coating acted as a barrier to the acid and solvent. However, due to the liquid present and the agitation caused by the mixer, this coating periodically was completely or partially washed off, thus exposing more rock for acidulation. The acidulation reaction frees the uranium for extraction. Immediately after the acidulation the uranium probably was present in the calcium sulfate phase as uranyl sulfate. The solvent then extracted it from there. The thinner the calcium sulfate layer was the easier it was to remove it from the rock particle. With a constant amount of calcium sulfate the thickness of this layer will be determined by the surface area necessary for it to cover. The greater the surface area (or the smaller the particle size), the thinner this layer will be, and the greater will be the uranium recovery.

Particle Size Studies Using a 1.81 Acidulation Ratio

The uranium extraction results using a 1.81 acidulation ratio throughout are presented in Table 3. These data show the very definite increase in uranium recovery with a decrease in particle size. All uranium recoveries in this work are on the basis of a 30 minute reaction time. The 30 minutes includes the time interval over which the acid was added. The effect of particle size on the uranium recovery as presented here, therefore, is valid only for a 30 minute reaction time. It appears likely that if the reaction time were extended the effect of particle size would decrease. This decrease would probably continue until the reaction time approached infinity, at which time the effect of particle size would approach zero. This is because at an infinite reaction time the reaction can progress to equilibrium regardless of the particle size. A graph of uranium recovery as a function of particle size appears in Figure 1. The graph shows that above 80 percent through 200 mesh, each succeeding incremental decrease in particle size produces a smaller increase in uranium recovery. This leveling off indicates that the curve becomes asymtotic at some particle size smaller than ninety-two percent

Table 3 Uranium recoveries using a 1.81 acidulation ratio

Run number	Particle size percent through 200 mesh	Percent uranium recovery based on solvent analysis	Average recovery for each particle size
E1	62	56.9	
E3	62	53.6	56.6
E5	62	59.2	
E2	77	67.7	
E4	77	65.5	66.0
E6	77	64.8	
E39	92	73.0	
E40	92	72.2	72.6

through 200 mesh. This then would put a practical limit on decreasing phosphate rock particle size. This practical limit would have to be based on the economics at the particular time in question.

It should be mentioned that in the particular case of the 92 percent through 200 mesh rock, at the 1.81 acidulation ratio, using 60 percent sulfuric acid produced a suspension of the solid products in the liquid phase. When this suspension was formed the uranium recovery was unaccountably poor, averaging 45.8 percent. This figure was considerably out of line with all other data. To avoid this suspension, 40 percent sulfuric acid was used for these two particular runs only. Using the 40 percent sulfuric acid prevented the formation of the suspension and increased the uranium recovery to an average of 72.6 percent. As illustrated by the curve of Figure 1 and also shown by a comparison to the same curve at a 2.50 acidulation ratio (Figure 4), this value fits in with all previous data.

As outlined in the Acidulation and Extraction Procedures section, at the end of every run the solvent was decanted from the solids, and the solids were washed with three 100 milliliter normal heptane washes. Therefore it must be kept in mind that the uranium recoveries are based on this particular procedure. It may be possible that further washings would

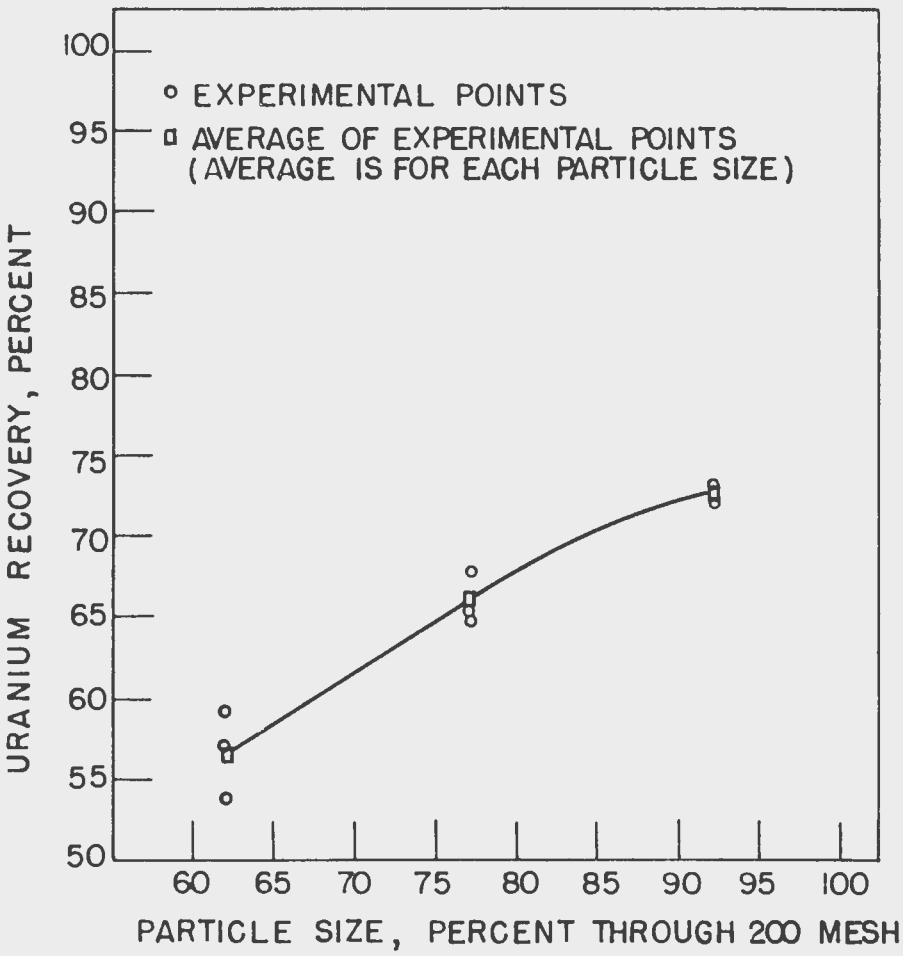

Figure 1. Effect of particle size on uranium recovery using a 1.81 acidulation ratio.

recover more of the solvent and increase the uranium recovery slightly. A single run at each particle size was made in which ten 100 milliliter normal heptane washes were used. The results of these runs showed that the extra seven washings had no effect whatsoever.

For each simultaneous reaction-extraction the available P_2O_5 was determined. The samples for analysis were taken immediately after the 30 minute mixing time. It was at this point that the solvent was separated from the superphosphate, which stopped any further uranium extraction. Therefore it was at this point that a measurement of the extent of lattice destruction was desired. An indication of lattice destruction was desired because the uranium is tied up in this lattice, and until it was destroyed the uranium was ot free to transfer into the solvent. The samples being analysed for the available P_2O_5 were weighed immersed in a water filled container so that there was no time lag error which might permit further conversion. The weighings were completed and the analyses were started in less than five minutes in every case.

The results of the P_2O_5 analyses for the 1.81 acidulation ratio, reported as percent conversion, are shown in Table 4. In Figure 2 a plot of P_2O_5 conversion as a function of particle size is shown. The curve's similar form to that of Figure 1 (uranium recovery versus particle size) further indicates that uranium recovery and P_2O_5 conversion are related. This supports the data of Wall (14) who correlated P_2O_5 conversion with uranium recovery.

The relation between uranium recovery and P_2O_5 conversion is plotted in Figure 3. The experimental points (curve A) show the expected linearity. Curve B is the mathematical relation between uranium recovery and P_2O_5 conversion as caluclated from the data of Wall (14). Wall found that six percent of the uranium could be recovered by a solvent leach of the unacidulated phosphate rock. Using this figure and assuming 100 percent uranium recovery at 100 percent P_2O_5 conversion, the equation of the line B was calculated to be

$$Y = 1.175X - 17.5$$

where Y equals percent uranium recovery and X equals percent P_2O_5 conversion. This assumes the relation to be a straight line which all experimental data have indicated thus far. The nearly identical slopes of curves A and B, 1.068 and 1.175 respectively, indicate that the relation is the same. The displacement between curves A and B will be discussed after the same plot at a 2.50 acidulation ratio is presented.

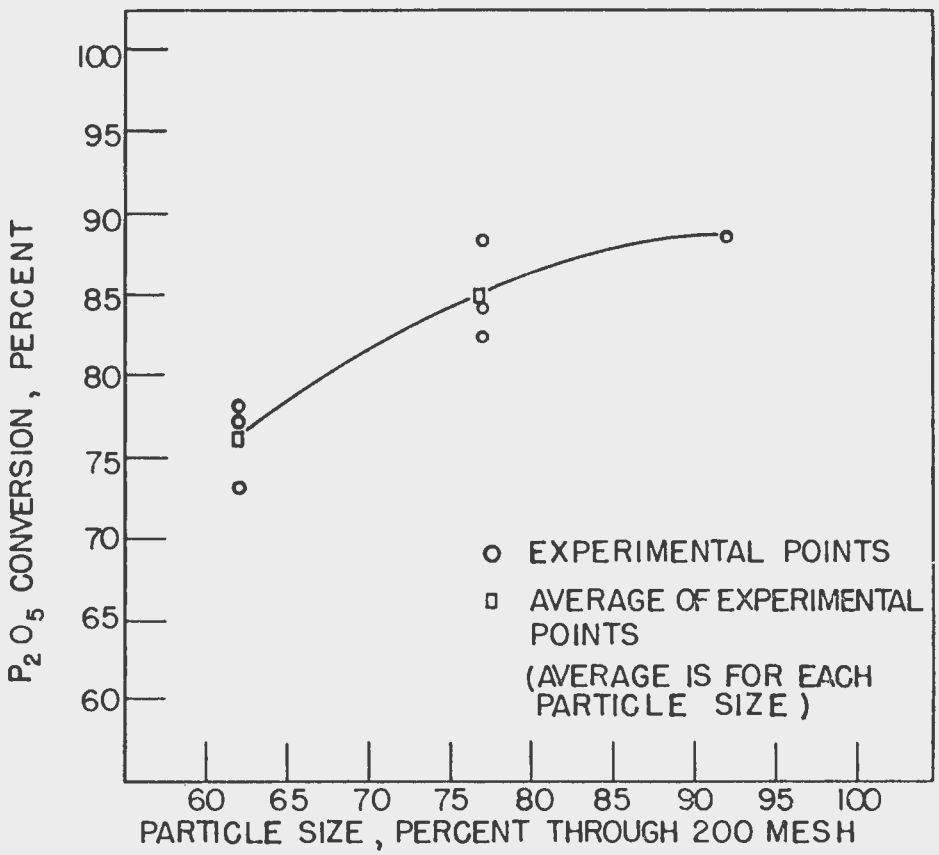

Figure 2. Effect of particle size on P_2O_5 conversion using a 1.81 acidulation ratio.

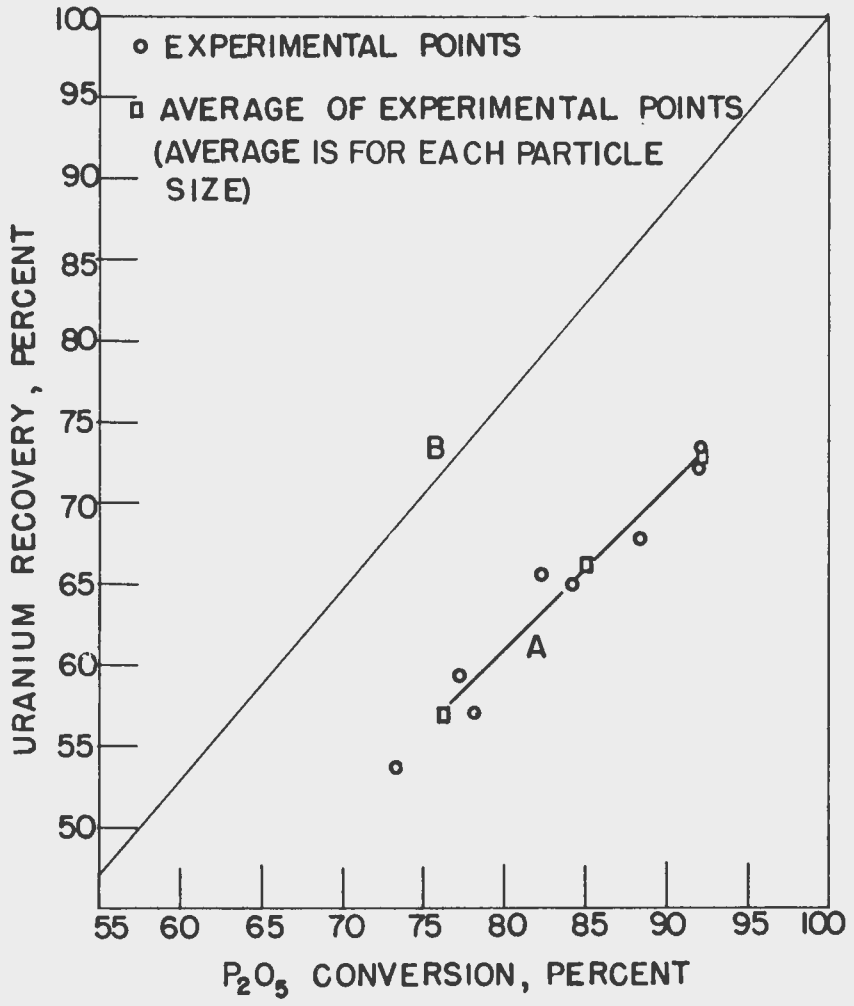

Figure 3. A. Experimental relation between uranium recovery and percent P_2O_5 conversion using a 1.81 acidulation ratio.

B. Mathematical relation between uranium recovery and percent P_2O_5 conversion.

Table 4. P_2O_5 conversions using a 1.81 acidulation ratio

Run number	Particle size percent through 200 mesh	Percent conversion	Average percent conversion
E1	62	78.0	
E3	62	73.2	76.1
E5	62	77.2	
E2	77	88.2	
E4	77	82.3	84.9
E6	77	84.1	
E39	92	Not run	
E40	92	88.5	88.5

Particle Size Studies Using a 2.50 Acidulation Ratio

The uranium extraction results using a 2.50 acidulation ratio during extraction and an overall 1.81 acidulation ratio are presented in Table 5. The initial percent recovery is based on the total uranium in the 250 grams of rock only. Actually this is the only rock that the solvent contacts. The overall percent recovery is based on the total uranium in the 250 grams plus that in the 95 grams of additional rock. A graphical presentation of these data is shown in Figure 4. In the following discussion of the 1.81 and 2.50 acidulation ratios, the comparison of the runs will be made using the initial uranium recovery for the 2.50 acidulation ratio unless the overall recovery is specifically indicated. This is done because the only difference in the reaction-extraction procedure up to that point has been the acidulation ratio.

The following points are to be noted in comparing the results at a 2.50 acidulation ratio (Table 5) with those using a 1.81 acidulation ratio throughout (Table 3):

1. The uranium recovery (considering the initial recovery for the 2.50 acidulation ratio) was less with the 2.50 than with the 1.81 acidulation ratio for corresponding particle sizes.

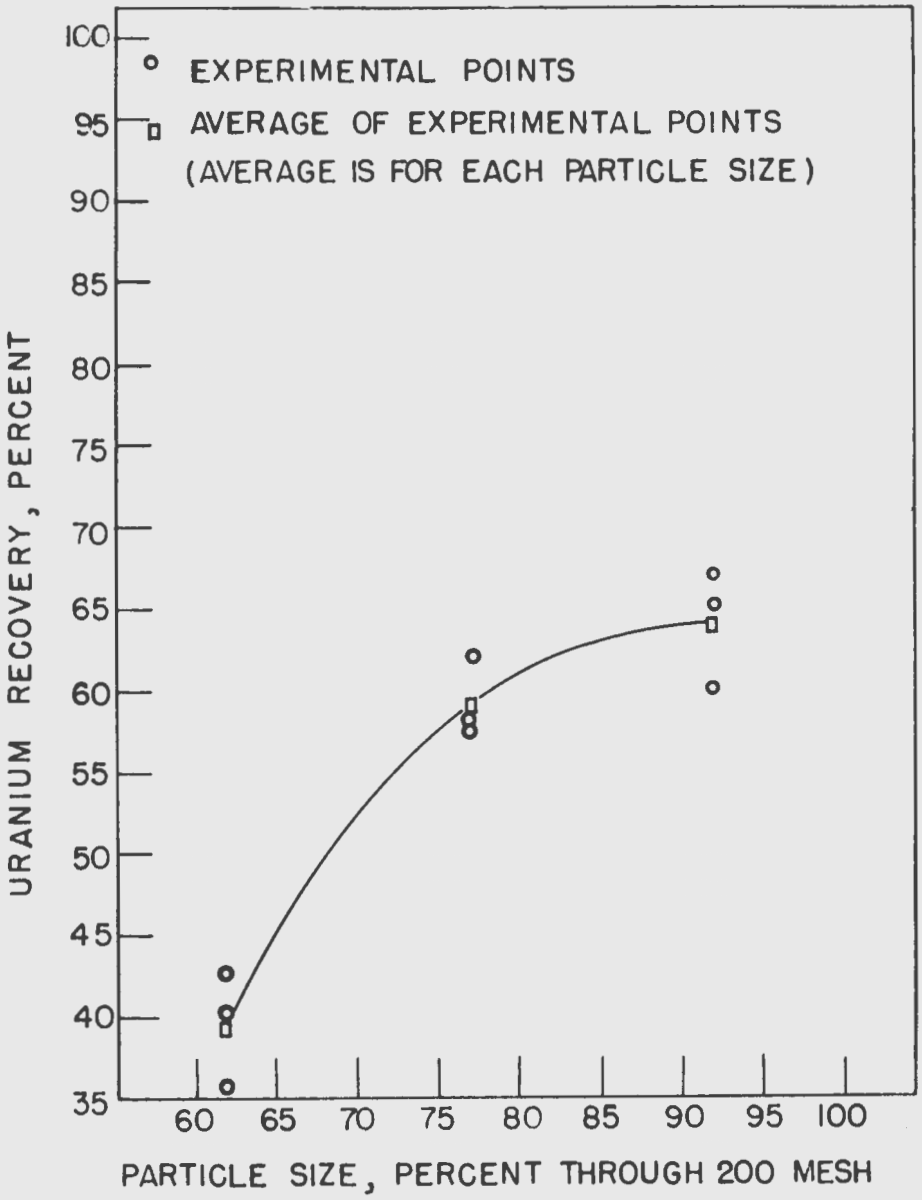

Figure 4. Effect of particle size on uranium recovery using a 2.50 acidulation ratio.

Table 5. Uranium recoveries using a 2.50 acidulation ratio

Run number	Particle size percent through 200 mesh	Percent uranium recovery based on solvent analysis	
		Initial	Overall
E7	62	39.9	28.9
E9	62	42.6	30.9
E11	62	35.3	25.6
Average	62	39.3	28.5
E8	77	61.8	44.8
E10	77	57.6	41.7
E12	77	57.9	41.9
Average	77	59.1	42.8
E20	92	67.0	48.5
E21	92	64.9	47.0
E23	92	60.0	43.5
Average	92	64.0	46.3

2. The P_2O_5 conversion was approximately five percent greater (10 percent greater for the 92 percent through 200 mesh rock) with the 2.50 acidulation ratio than with the 1.81 acidulation ratio at corresponding particle sizes.

3. The effect of particle size appeared to be greater (considering initial recovery only) with the 2.50 acidulation ratio.

A discussion of statements 1 and 2 follows: as far as the uranium extraction into the solvent was concerned the only difference between the 1.81 and the 2.50 runs was that a greater amount of acid was added over the same 10 minute interval. It was thought that this additional acid would more quickly and more completely break down the lattice structure, thus releasing more uranium to be absorbed by the solvent. Apparently the effect on the lattice structure was as expected. This can be seen by observing the greater P_2O_5 conversion at the 2.50 acidulation ratio than at the 1.81 acidulation ratio, as illustrated in Tables 6 and 4, respectively. Plotting percent P_2O_5 conversion versus particle size at the 2.50 acidulation ratio, Figure 5, gives the same characteristic curve obtained with the 1.81 acidulation ratio. In this case, however, the curve levels off at a P_2O_5 conversion approaching 100 percent. If the uranium was also released as theorized, it is evident that it was not recovered by the solvent. This is shown by a comparison of curve A of Figures 3 and 6, which illustrate uranium recovery as a function of P_2O_5 conversion for a 1.81 and a 2.50 acidulation ratio respectively.

Now consider the two main differences in the 1.81 and the 2.50 runs. A greater quantity of acid was added to the 250 grams of phosphate rock to reach a 2.50 acidulation ratio. For the 2.50 acidulation ratio 246 milliliters were used; for the 1.81 only 178 milliliters were used. With the 1.81 acidulation ratio the reaction between the rock and the acid may be represented as:

$$Ca_{10}F_2(PO_4)_6 + 7H_2SO_4 + 3H_2O \longrightarrow 3Ca(H_2PO_4)_2 \cdot H_2O + 7CaSO_4 + 2HF.$$

With the 2.50 acidulation ratio the reaction may be represented as:

$$Ca_{10}F_2(PO_4)_6 + 10\ H_2SO_4 \longrightarrow 6H_3PO_4 + 10CaSO_4 + 2HF$$

In this case the phosphoric acid then reacted with more phosphate rock to form the soluble or so-called available some calcium phosphate, $Ca(H_2PO_4)_2$. The difference to note in the two basic reactions is that for the 2.50 acidulation ratio 10 moles of insoluble calcium sulfate were formed from each fluorapatite molecule compared to only seven for the 1.81 acidulation ratio. This calcium sulfate existed in its various different forms of hydration, although principally thought to have been gypsum, $CaSO_4 : 2H_2O$. It was insoluble and is thought to have formed a layer or loose coating around the phosphate rock particle. As discussed earlier, the agitation in the reaction-extraction beaker periodically washed part or all of this coating off, which allowed more acid to react and form more calcium sulfate. This cycle was constantly repeated throughout the reaction.

The greater P_2O_5 conversions at the 2.50 acidulation ratio are explained by the greater quantity of sulfuric acid used. The greater P_2O_5 conversions also indicate that a greater amount of uranium was freed from the fluorapatite lattice. However, the uranium recoveries were lower at the 2.50 than at the

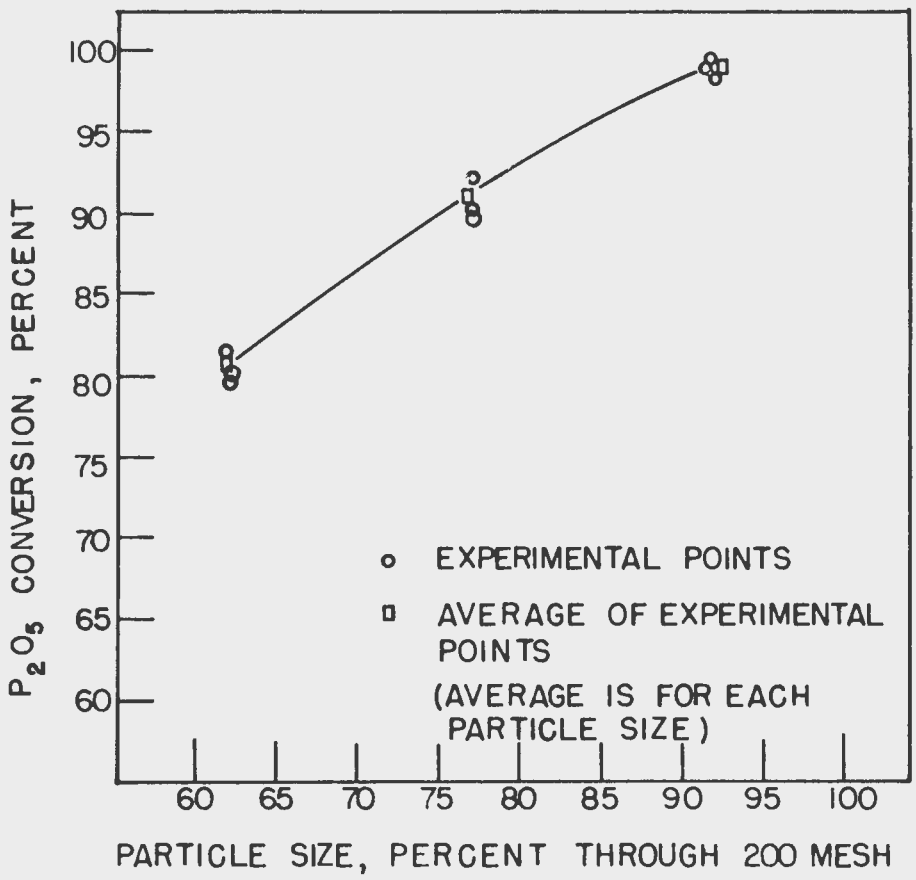

Figure 5. Effect of particle size on P_2O_5 conversion using a 2.50 acidulation ratio.

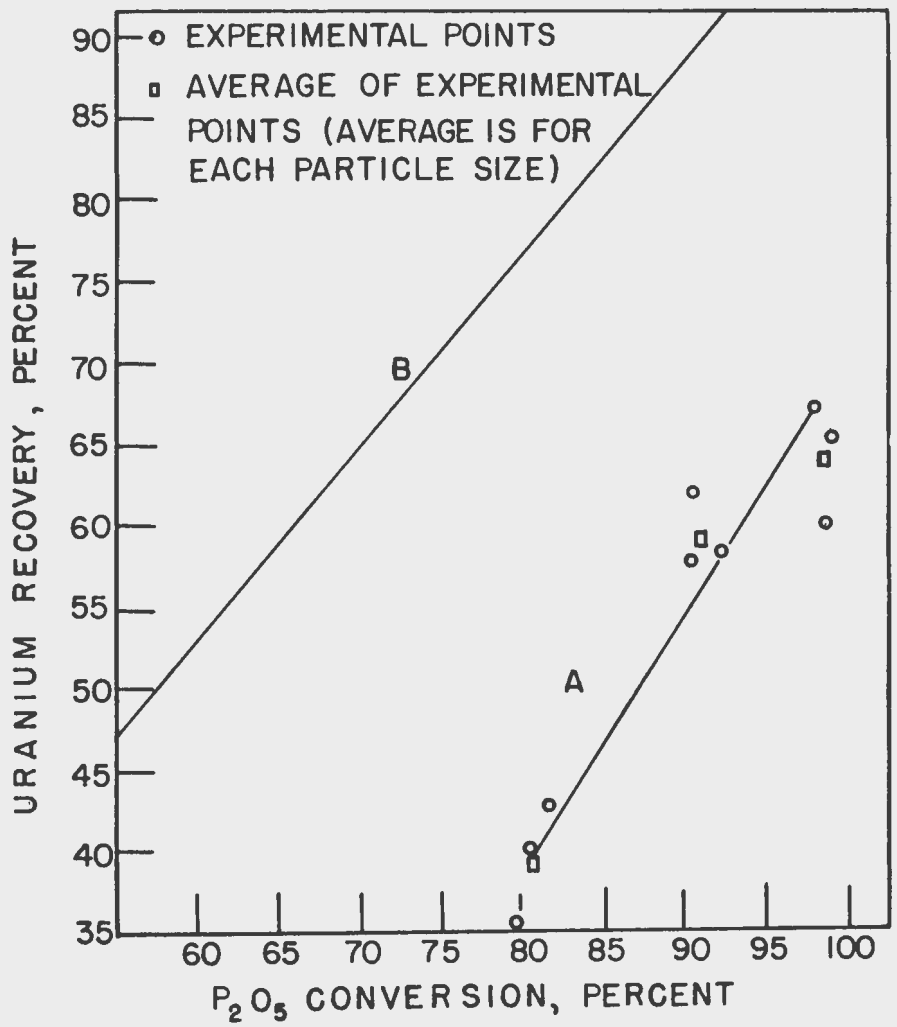

Figure 6. A. Experimental relation between uranium recovery and percent P_2O_5 conversion using a 2.50 acidulation ratio.

B. Mathematical relation between uranium recovery and percent P_2O_5 conversion.

Table 6. P_2O_5 conversions using a 2.50 acidulation ratio

Run number	Particle size percent through 200 mesh	Percent conversion	Average percent conversion
E7	62	80.3	
E9	62	81.6	80.5
E11	62	79.7	
E8	77	90.6	
E10	77	90.3	90.9
E12	77	91.9	
E20	92	98.3	
E21	92	99.1	98.7
E23	92	98.7	

1.81 acidulation ratio. This may be explained by the greater amount of calcium sulfate formed. As discussed earlier, immediately after the reaction the uranium probably existed in the calcium sulfate phase as uranyl sulfate. It was from here that the solvent extracted the uranium. It is possible that the calcium sulfate could have acted as a quite zone where the O.P.P.A. was allowed to coalesce and be trapped as an inert drop. Thus, further reaction could proceed without increasing the uranium recovery. This, of course, could have occurred at the 1.81 acidulation ratio as well as at the 2.50. However, with the 2.50 acidulation ratio there was 10/7 or nearly 1.5 times as much calcium sulfate surrounding the uranium as with the 1.81 acidulation ratio. This provides additional calcium sulfate to trap additional solvent. Also, the larger amount of calcium sulfate would further physically block the solvent from the uranyl sulfate. Therefore, it would seem logical that the extraction of the uranium would be more difficult and result in lower recovery.

The second main difference between the 2.50 and 1.81 acidulation ratios was the faster acid addition rate for the 2.50. For the 1.81 acidulation ratio the acid addition rate was 0.297 milliliters per second; for the 2.50 it was 0.410 milliliters per second. In both cases the required amount of acid was added over a 10 minute interval. The higher rate for the 2.50 was necessary to add the larger amount of acid over the same time interval.

It was thought that this higher acid addition rate might have something to do with the lower uranium recoveries obtained with the 2.50 acidulation ratio. Thus an entire series of runs was made at a 2.50 acidulation ratio for both the 0.297 and the 0.410 milliliters per second acid addition rates. The data of Tables 5 and 6 are based on the 0.410 milliliters per second rate.

To add all the acid required for a 2.50 acidulation ratio at 0.297 milliliters per second required 13.8 minutes instead of the 10 minutes needed to reach a 1.81 acidulation ratio at this rate. It was felt that if the acid was added at 0.297 milliliters per second for the 2.50 acidulation ratio, after 10 minutes the procedures for both the 1.81 and the 2.50 would have been exactly the same, and therefore, the uranium recovery for the 2.50 acidulation ratio would be at least as good as with the 1.81 acidulation ratio. It was thought that the additional acid added in the last 3.8 minutes would have no deleterious effect, and could even benefit the extraction by further reaction with the rock. However, as the data in Table 7 indicates, such was not the case. The slower acid addition rate did not affect the uranium recoveries significantly; rather, as discussed earlier, the difference in the uranium recoveries is probably due to the greater amount of calcium sulfate formed.

In a further effort to determine the cause of the lower uranium recoveries at the 2.50 acidulation ratio, three more runs were made at a 2.50 acidulation ratio using 62 percent through 200 mesh phosphate rock. The object of these runs was to determine how much uranium, if any, was being lost into the aqueous phase which was formed only with the 2.50 acidulation ratio. This aqueous phase consisted mostly of phosphoric acid and a small amount of unreacted sulfuric acid. Its volume varied between 30 and 60 milliliters for runs of this size. Immediately after the 30 minute reaction-extraction the aqueous phase was analysed fluorimetrically for uranium using a standard curve developed by Wall (14). Then it was contacted for one minute with each of two 100 milliliter quantities of fresh 10 percent O.P.P.A. in normal heptane. These solvent phases were combined and also analysed for uranium. The results of these runs are shown in Table 8. These data show that only about one percent of the uranium went into the aqueous phase. Thus, this does not account for the lower uranium recoveries obtained with a 2.50 acidulation ratio. It appears once again, then, that the explanation lies in the greater amount of calcium sulfate formed with a 2.50 acidulation ratio.

There is another point to consider as a possible explanation for part of this lower uranium recovery. The uranium material balances, shown in Table 9, were on the low side for all runs made with a 2.50 acidulation ratio. This was not true at a 1.81 acidulation ratio. Therefore, if the uranium unaccounted for would have gone into the solvent, the uranium recoveries at the 2.50 acidulation ratio would all increase, and perhaps approach the reocveries obtained at the 1.81 acidulation ratio.

Table 7. Comparison of acid addition rates at a 2.50 acidulation ratio

Particle size percent through 200 mesh	0.410 ml./sec.			0.297 ml./sec.		
	Run number	Initial percent uranium recovery	Percent P_2O_5 conversion	Run number	Initial percent uranium recovery	Percent P_2O_5 conversion
62	E7	39.9	80.3	E25	32.4	72.5
62	E9	42.6	81.6	E28	29.8	76.3
62	E11	35.3	79.5	E31	37.0	73.4
Average for 62		39.3	80.5		33.1	74.1
77	E8	61.8	90.6	E26	44.7	79.9
77	E10	57.6	90.3	E29	52.0	86.6
77	E12	57.9	91.9	E32	49.9	88.0
Average for 77		59.1	90.9		48.9	88.2
92	E20	67.0	98.3	E27	63.1	98.7
92	E21	64.9	99.1	E37	67.6	Not run
92	E23	60.0	98.7			
Average for 92		64.0	98.7		65.3	98.7

Table 8. Percent uranium in the aqueous phase at a 2.50 acidulation ratio

Run Number	Initial percent uranium recovery	Initial percent uranium in aqueous phase based on analysis of:	
		Aqueous phase	Solvent
E41	36.2	0.79	1.08
E42	32.7	1.36	1.67
E43	33.9	1.08	1.55

Consider now the displacement between curves A and B in Figures 3 and 6. According to curve B in Figure 3, for example, at 85 percent P_2O_5 conversion the uranium recovery should have been 82 percent. However, at 85 percent P_2O_5 conversion the experimental uranium recovery was only 67 percent. For the 2.50 acidulation ratio (Figure 6) this deficiency is even greater. This deficiency may be explained by the calcium sulfate coating and the 30 minute reaction-extraction time. At a given P_2O_5 conversion a certain amount of uranium will be freed for extraction and a certain amount of calcium sulfate will be formed (depending on the acidulation ratio). However, it will require a certain amount of time for the solvent, with the aid of the agitation, to reach all the uranium dispersed throughout the calcium sulfate. If an infinite mixing time was used it is felt that curve A would approach curve B. The greater deficiency with the 2.50 acidulation ratio (Figure 6) results from the greater amount of calcium sulfate formed.

Statement 3 refers to the relative effect of particle size at the two different acidulation ratios. In decreasing the particle size from 62 to 92 percent through 200 mesh at the 2.50 acidulation ratio an increase of 24.7 percent uranium recovery was obtained; for the same particle size decrease at a 1.81 acidulation ratio an increase of only 16.0 percent uranium recovery was obtained. It should be kept in mind that this effect of particle size is valid only for a 30 minute reaction time. Consider again the low uranium material balances obtained with the 2.50 acidulation ratio. It is possible that the unaccounted for uranium may have something to do with the apparent greater effect of particle size at the 2.50 acidulation ratio.

The uranium recoveries have all been reported from analyses of the solvents. To make a uranium material balance the superphosphates were also analysed. The uranium material balances are shown in Table 9. An acceptable uranium material balance was considered to be plus or minus 10 percent. For the 1.81 acidulation ratio the material balances checked very well. For the 2.50 acidulation ratio consistently low results were obtained. There is no explanation for this at present.

Table 9. Uranium material balances

Run number	Acidulation ratio	Particle size Percent through 200 mesh	Acid addition rate ml./sec.	Uranium put in Grams x 100	Uranium accounted for Grams x 100	Percent accounted for
E1	1.81	62	0.297	4.60	4.65	101.3
E2	1.81	77	0.297	4.60	4.70	102.4
E3	1.81	62	0.297	4.60	4.57	99.6
E4	1.81	77	0.297	4.60	5.02	109.4
E5	1.81	62	0.297	4.60	4.77	103.9
E6	1.81	77	0.297	4.60	4.71	102.6
E7	2.50	62	0.410	6.34	5.80	91.8
E8	2.50	77	0.410	6.34	5.93	93.7
E9	2.50	62	0.410	6.34	5.60	88.5
E10	2.50	77	0.410	6.34	5.53	87.4
E11	2.50	62	0.410	6.34	5.36	84.7
E12	2.50	77	0.410	6.34	5.55	87.7
E20	2.50	92	0.410	6.34	5.82	91.7
E21	2.50	92	0.410	6.34	5.74	90.4
E23	2.50	92	0.410	6.34	5.48	86.3
E25	2.50	62	0.297	6.34	5.06	79.7
E26	2.50	77	0.297	6.34	6.67	105.1
E27	2.50	92	0.297	6.34	5.62	88.6
E28	2.50	62	0.297	6.34	4.23	66.7
E29	2.50	77	0.297	6.34	5.21	82.0

Table 9. (Continued)

Run number	Acidulation ratio	Particle size Percent through 200 mesh	Acid addition rate ml./sec.	Uranium put in Grams x 100	Uranium accounted for Grams x 100	Percent accounted for
E31	2.50	62	0.297	6.34	4.42	69.7
E32	2.50	77	0.297	6.34	4.75	74.8
E37	2.50	92	0.297	6.34	5.43	85.5
E39	1.81	92	0.297	4.60	4.28	93.0
E40	1.81	92	0.297	4.60	4.20	91.4
E41	2.50	62	0.410	6.34	4.74	74.6
E42	2.50	62	0.410	6.34	4.78	75.3
E43	2.50	62	0.410	6.34	4.89	77.0

CONCLUSIONS AND RECOMMENDATIONS

Following are the conclusions drawn from the results of this work:

1. The recovery of the uranium in phosphate rock in a 30 minute reaction-extraction during the production of normal superphosphate increases significantly with a decreasing phoshphate rock particle size.

2. The process based on an initial over-acidulation ratio (2.50) does not appear to have any advantage over the process based on the normal acidulation ratio (1.81). Even if the initial reaction permitted the recovery of 100 percent of the uranium, the overall uranium recovery would be no better than that obtained with a 1.81 acidulation ratio. Furthermore, the 2.50 acidulation process requires an additional processing step which would increase the overall cost of the process.

3. Uranium recovery in a 30 minute reaction-extraction is not affected by varying the acid addition rate at a 2.50 acidulation ratio.

4. The relative effect of phosphate rock particle size on the uranium recovery obtained in a 30 minute reaction-extraction appears to be greater with a 2.50 acidulation ratio than with a 1.81 acidulation ratio.

It is recommended that further work be done on the recovery of the O.P.P.A. solvent from the superphosphate. A study of this problem was begun by Wall (14), who investigated drying as a possible method of solvent recovery. It is felt that any further work on the recovery of uranium from normal superphosphate should be done on a pilot plant scale.

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